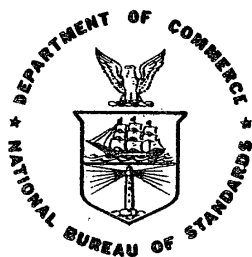# NBSIR 77-1278

The Air Density Equation and the Transfer of the Mass Unit

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ABSTRACT

A new formulation of the equation used for the calculation of air
density has been developed. The Quinn, Colclough and Chandler
value of the gas constant, currently accepted values of the atomic
weights, and recent determinations of the abundances of the various
constituents of air have been used. The abundance of carbon dioxide
has been treated as a variable and a factor enabling convenient
adjustment of the apparent molecular weight of air for deviation
of carbon dioxide abundance from a background value has been derived.
A new table of compressibility factor for the range of pressure and
temperature of interest in standards laboratories has been calculated
using recently determined values of virial coefficients. The enhance-
ment factor, which has usually been ignored in air density equations,
has been explicitly included in the equation; a table of enhancement
factor has been calculated using a simple equation fitted to values
in the range of pressure and temperature of interest. A table of the
saturation water vapor pressure has been included; a simple equation
for the calculation of saturation water vapor pressure has been fitted.
Uncertainties, random and systematic, in the parameters and in the
measurement of environmental variables and consequent uncertainties
in calculated air density have been estimated.

Application of the equation to air buoyancy determination and the
transfer of the mass unit at the various national standards
laboratories has been made.

Key Words: Air buoyancy, air density, mass unit transfer, real gas
equation.

1. INTRODUCTION

The transfer of the mass value from one object, such as the International Prototype Kilogram, to another object is accomplished by comparison of the objects by means of a balance. The difference in buoyant force on the two objects is proportional to the difference in their displacement volumes and to the air density. The air density is conventionally calculated using an equation based on the equation of state of an air-water vapor mixture. A new formulation of the air density equation is developed below.

2. DEVELOPMENT OF THE AIR DENSITY EQUATION

The total pressure, P, the total volume, V, and the absolute temperature, T, of a mixture of ideal gases are related by the ideal gas equation,

$$PV = nRT, \tag{1}$$

where $\underline{n}$ is the number of moles of the mixture and $\underline{R}$ is the universal gas constant. In terms of density, ρ, rather than volume, Eq. (1) becomes

$$P = \rho \frac{R}{M} T, \tag{2}$$

where $\underline{M}$ is the apparent molecular weight of the mixture.

For a mixture of dry air (indicated by subscript a) and water vapor (subscript e), M is the apparent molecular weight of the air-water vapor mixture,

Since

$$M = \frac{m}{n} = \frac{m_a + m_e}{n_a + n_e}, \tag{3}$$

where $\underline{m}$ is the mass of the mixture and $\underline{n}$ is the number of moles of the mixture.

$$M = \frac{n_a M_a + n_e M_e}{n_a + n_e} = \frac{M_a \left(1 + \dfrac{n_e M_e}{n_a M_a}\right)}{\left(1 + \dfrac{n_e}{n_a}\right)}. \tag{4}$$

By introducing the water vapor mixing ratio, r:

$$r = \frac{\text{mass of water vapor}}{\text{mass of dry air}} = \frac{m_e}{m_a} = \frac{n_e M_e}{n_a M_a}, \tag{5}$$

Eq. (4) becomes

$$M = \frac{M_a(1 + r)}{\left(1 + \dfrac{r}{M_e/M_a}\right)} . \qquad (6)$$

By designating the ratio $\dfrac{M_e}{M_a}$ by ϵ, Eq. (6) becomes

$$M = \frac{M_a(1 + r)}{(1 + \dfrac{r}{\epsilon})} , \qquad (7)$$

and by substituting Eq. (7) in Eq. (2), we find that

$$P = \rho \frac{R}{M_a} T \left(\frac{1 + \dfrac{r}{\epsilon}}{1 + r}\right). \qquad (8)$$

The effective vapor pressure, e', of water <u>in moist air</u> is defined [1] by:

$$e' = \frac{r}{(\epsilon + r)} P , \qquad (9)$$

therefore,

$$r = \frac{\epsilon e'}{(P - e')} \qquad (10)$$

and Eq. (8) becomes

$$P = \rho \frac{R}{M_a} T \left[\frac{1}{1 + (\epsilon-1)\dfrac{e'}{P}}\right] . \qquad (11)$$

Eq. (11) is the <u>ideal</u> gas equation for a mixture of dry air and water vapor with a water vapor pressure of e'. If the air-water vapor mixture behaved as a mixture of ideal gases,

$$\frac{P}{\rho \dfrac{R}{M_a}T\left[\dfrac{1}{1 + (\epsilon-1)\dfrac{e'}{P}}\right]} = Z = 1, \qquad (12)$$

where $\underline{Z}$ is the compressibility factor. Since Z is not, in general, equal to 1, the mixture is not ideal. The magnitude of the non-ideality is reflected in the departure of the value of Z from 1 and Eq. (12) becomes

2

$$P = \rho \frac{R}{M_a} TZ \left[\frac{1}{1 + (\varepsilon - 1)\frac{e'}{P}} \right] . \qquad (13)$$

Eq. (13) is the <u>real</u> gas equation for a mixture of dry air and water vapor. By rearranging Eq. (13), the expression for density is

$$\rho = \frac{PM_a}{RTZ} \left[1 + (\varepsilon - 1)\frac{e'}{P} \right] . \qquad (14)$$

Eq. (14) is the form of the equation to be used to calculate air density.

3. SPECIFICATION OF THE VALUES OF THE PARAMETERS IN EQ. (14)

3.1 Universal Gas Constant, R.

The value of the molar gas constant, R, listed in a compilation by Cohen and Taylor [2] is 8.31441 ± 0.00026 J mol^{-1} K^{-1}, where the uncertainty corresponds to 1 standard deviation. Recently, Quinn, Colclough and Chandler (QCC) [3] made a new determination of R by measuring the speed of sound in argon by means of an acoustic interferometer. Their value is 8315.73 ± 0.17 JK^{-1} kmol^{-1}, where the uncertainty quoted is "one statistical standard error in a fit of 95 degrees of freedom." Quinn et al concluded that a real systematic difference exists between their value and the Cohen and Taylor value, and that they were unable to point to any single factor which could be unambiguously identified as the source of the disagreement. Gammon [4] recently deduced a value of R from measurements of the velocity of sound in helium. His latest reported value [5] is 8315.31 ± 0.35 JK^{-1} kmol^{-1}, which is in good agreement with the QCC value.

The difference between the Cohen and Taylor and the QCC values, if it were considered to be a systematic uncertainty, would correspond to a systematic relative uncertainty in the calculated value of ρ of 159 p.p.m., a quite significant contribution. One is thus confronted with the necessity to choose between two significantly discordant values. The long-term alternative would be to await a new, definitive experimental determination of R (plans are presently being made at NBS to make a definitive determination of R). We choose at present to use the QCC value, with the realization that in the future it might be replaced by a new value, at which time the formulation developed in the present work would be modified to accommodate the new value.

3.2 Apparent Molecular Weight of Air, M_a

The apparent molecular weight of dry air, M_a, is calculated using the relationship

$$M_a = \frac{\sum\limits_{i=1}^{k} M_i x_i}{\sum\limits_{i=1}^{k} x_i}, \qquad (15)$$

where each M_i is the molecular weight of an individual constituent and x_i is the corresponding mole fraction. The molecular weights and mole fractions of the constituents of dry air are tabulated in table 1. Other constituents are present in abundances which are negligible for the present application.

TABLE 1. NORMAL COMPOSITION OF CLEAN, DRY
ATMOSPHERIC AIR NEAR SEA LEVEL

Constituent	Abundance (mole fraction)	Molecular Weight
Nitrogen (N_2)	0.78102	28.0134
Oxygen (O_2)	0.20946	31.9988
Carbon Dioxide (CO_2)	0.00033	44.0098
Argon (A)	0.00916	39.948
Neon (Ne)	0.00001818	20.179
Helium (He)	0.00000524	4.00260
Krypton (Kr)	0.00000114	83.80
Xenon (Xe)	0.000000087	131.30
Hydrogen (H_2)	0.0000005	2.0158
Methane (CH_4)	0.000002	16.0426
Nitrous Oxide (N_2O)	0.0000005	44.0128

The values of the atomic weights of the elements are taken from reference [6] and are based on the carbon-12 scale. The molecular weights are taken to be the sums of the atomic weights of the appropriate elements.

The value for the abundance of oxygen is taken from reference [7].

4

The value for the abundance of carbon dioxide is taken from a recent unpublished compilation of data on atmospheric concentration of carbon dioxide at seven locations throughout the world. It must be emphasized that 0.00033 is the mole fraction of CO_2 in the atmosphere and should be considered to be a "background" value. The mole fraction of CO_2 in laboratories, which is of course the value of interest here, is in general greater than 0.00033 and is variable. For example, three samples of air taken from a glove box in the Mass Laboratory at NBS had a mean value of 0.00043, and four samples of laboratory air taken at the National Center for Atmospheric Research in Boulder, Colorado had a mean value of 0.00080. Clearly, then, the optimum utilization of the air density calculation would necessitate a measurement of CO_2 abundance on an air sample taken at the time of the mass comparison.

One of the options one has in dealing with the variability of CO_2 abundance is to select a reference level (for example, 0.00033 or 0.00043) and to provide an adjustment to M_a to account for known departures from the reference level. Gluekauf [8], in discussing the variation of the abundance of oxygen in the atmosphere, stated that "all major variations of the O_2 content must result from the combustion of fuel, from the respiratory exchange of organisms, or from the assimilation of CO_2 in plants. The first process does not result in more than local changes of O_2 content, while the latter two processes, though locally altering the CO_2/O_2 ratio, leave their sum unchanged." The assumed constancy of the sum of the O_2 and CO_2 abundance simplifies the adjustment of M_a to account for departures from the CO_2 reference level and simplifies the estimation of the uncertainty in air density due to an uncertainty in CO_2 abundance. The constancy of the sum is expressed by the equation (for convenience, the subscript i has been replaced by the chemical symbol):

$$x_{CO_2} + x_{O_2} = \text{constant} = 0.20979 . \tag{16}$$

The contribution of O_2 and CO_2 to the apparent molecular weight of dry air is

$$M_{O_2} x_{O_2} + M_{CO_2} x_{CO_2} = 31.9988\ x_{O_2} + 44.0098\ x_{CO_2} . \tag{17}$$

From Eq. (16),

$$x_{O_2} = 0.20979 - x_{CO_2} . \tag{18}$$

The right side of Eq. (17) becomes

$$31.9988 \left[0.20979 - x_{CO_2} \right] + 44.0098\ x_{CO_2} , \tag{19}$$

5

thus,

$$M_{O_2} x_{O_2} + M_{CO_2} x_{CO_2} = 12.011 \ x_{CO_2} + 6.7130 \quad . \tag{20}$$

Therefore

$$\delta(M_a) = \delta \left[M_{O_2} x_{O_2} + M_{CO_2} x_{CO_2} \right] = 12.011 \ \delta \left(x_{CO_2} \right) , \tag{21}$$

that is, the variation in M_a due to a variation in CO_2 abundance is equal to 12.011 (the atomic weight of carbon) multiplied by the variation in CO_2 abundance. The variation in M_a due to the difference between the reference levels 0.00033 and 0.00043 is thus 0.0012 g mol^{-1} which corresponds to a relative variation of 41 p.p.m. in M_a and a corresponding relative variation of 41 p.p.m. in air density.

The adjustment of M_a to account for a departure of the CO_2 abundance from the reference level becomes

$$12.011 \left[x_{CO_2} - \left(x_{CO_2} \right)_o \right] , \tag{22}$$

where the subscript o indicates the reference level. The adjusted M_a for a reference level of 0.00033 becomes

$$M_a = M_{a_{033}} + 12.011 \left[x_{CO_2} - 0.00033 \right] , \tag{23}$$

where $M_{a_{033}}$ is the apparent molecular weight of dry air with a CO_2 mole fraction of 0.00033 (as indicated by the subscript 033).

The value for the abundance of argon in dry air, 0.00916, is that calculated from the mass spectrometric determination of the ratio of argon to argon and nitrogen by Hughes [9].

The value for the abundance of nitrogen was arrived at by the usual practice of inferring nitrogen abundance to be the difference between unity and the sum of the mole fractions of the other constituents.

The abundances of the constituents neon through nitrous oxide in table 1 were taken to be equal to the parts per volume concentration in U.S. Standard Atmosphere, 1962 [10].

From the data of table 1, the apparent molecular weight of dry air with a CO_2 mole fraction of 0.00033 is calculated by Eq. (15) to be 28.963.

6

3.3 Compressibility Factor, Z

The compressibility factor is computed using the virial equation of state of an air-water vapor mixture expressed as a power series in reciprocal molar volume,

$$Z = \frac{Pv}{RT} = 1 + \frac{B_{mix}}{v} + \frac{C_{mix}}{v^2} + \ldots \ldots , \qquad (24)$$

and expressed as a power series in pressure,

$$Z = \frac{Pv}{RT} = 1 + B'_{mix} P + C'_{mix} P^2 + \ldots \ldots , \qquad (25)$$

where v is the molar volume, B_{mix} and B'_{mix} are second virial coefficients and C_{mix} and C'_{mix} are third virial coefficients for the mixture. The virial coefficients of the pressure series are related to the virial coefficients of the volume power series by

$$B'_{mix} = \frac{B_{mix}}{RT} \qquad (26)$$

and

$$C'_{mix} = \frac{C_{mix} - B^2_{mix}}{(RT)^2} . \qquad (27)$$

Each mixture virial coefficient is a function of the mole fractions of the individual constituents and the virial coefficients for the constituents. The latter are functions of temperature only.

The second interaction (cross) virial coefficient of moist air, B_{aw}, is one of the contributors to B'_{mix} and expresses the effects of interaction between an air molecule and a water molecule. The values of B_{aw} used in the calculation of Z are experimental values which strictly apply to CO_2-free air.

Using equations (34) and (35), below, and the virial coefficients [11, 15] provided by Hyland, a table of compressibility factor, Z, for CO_2-free air, table 2, has been generated.

7

TABLE 2   COMPRESSIBILITY FACTOR, Z, FOR CO$_2$-FREE AIR

Temperature (Celsius)	Pressure (pascals)	(mm Hg)	Relative Humidity in Percent 0	25	50	75	100
15.0	70000	525.0	.99971	.99970	.99968	.99967	.99965
	75000	562.5	.99969	.99968	.99966	.99965	.99963
	80000	600.0	.99966	.99966	.99964	.99963	.99961
	85000	637.6	.99964	.99963	.99962	.99961	.99959
	90000	675.1	.99962	.99961	.99960	.99959	.99957
	95000	712.6	.99960	.99959	.99958	.99957	.99955
	100000	750.1	.99958	.99957	.99956	.99955	.99953
	101325	760.0	.99958	.99957	.99956	.99954	.99953
	105000	787.6	.99956	.99955	.99954	.99953	.99951
	110000	825.1	.99954	.99953	.99952	.99951	.99949
16.0	70000	525.0	.99971	.99970	.99969	.99967	.99965
	75000	562.5	.99969	.99968	.99967	.99965	.99963
	80000	600.0	.99967	.99966	.99965	.99963	.99962
	85000	637.6	.99965	.99964	.99963	.99961	.99960
	90000	675.1	.99963	.99962	.99961	.99959	.99958
	95000	712.6	.99961	.99960	.99959	.99958	.99956
	100000	750.1	.99959	.99958	.99957	.99956	.99954
	101325	760.0	.99959	.99958	.99956	.99955	.99953
	105000	787.6	.99957	.99956	.99955	.99954	.99952
	110000	825.1	.99955	.99954	.99953	.99952	.99950
17.0	70000	525.0	.99972	.99971	.99970	.99968	.99966
	75000	562.5	.99970	.99969	.99968	.99966	.99964
	80000	600.0	.99968	.99967	.99966	.99964	.99962
	85000	637.6	.99966	.99965	.99964	.99962	.99960
	90000	675.1	.99964	.99963	.99962	.99960	.99958
	95000	712.6	.99962	.99961	.99960	.99958	.99956
	100000	750.1	.99960	.99959	.99958	.99956	.99954
	101325	760.0	.99960	.99959	.99957	.99956	.99954
	105000	787.6	.99958	.99957	.99956	.99954	.99953
	110000	825.1	.99956	.99955	.99954	.99952	.99951
18.0	70000	525.0	.99973	.99972	.99970	.99968	.99966
	75000	562.5	.99971	.99970	.99968	.99966	.99964
	80000	600.0	.99969	.99968	.99966	.99964	.99962
	85000	637.6	.99967	.99966	.99964	.99963	.99960
	90000	675.1	.99965	.99964	.99962	.99961	.99959
	95000	712.6	.99963	.99962	.99961	.99959	.99957
	100000	750.1	.99961	.99960	.99959	.99957	.99955
	101325	760.0	.99961	.99960	.99958	.99957	.99955
	105000	787.6	.99959	.99958	.99957	.99955	.99953
	110000	825.1	.99957	.99956	.99955	.99953	.99951

Table 2 (Continued)

Temperature (Celsius)	Pressure (pascals)	(mm Hg)	Relative Humidity in Percent 0	25	50	75	100
19.0	70000	525.0	.99973	.99972	.99971	.99968	.99966
	75000	562.5	.99972	.99970	.99969	.99967	.99964
	80000	600.0	.99970	.99968	.99967	.99965	.99963
	85000	637.6	.99968	.99967	.99965	.99963	.99961
	90000	675.1	.99966	.99965	.99963	.99961	.99959
	95000	712.6	.99964	.99963	.99961	.99960	.99957
	100000	750.1	.99962	.99961	.99959	.99958	.99956
	101325	760.0	.99962	.99960	.99959	.99957	.99955
	105000	787.6	.99960	.99959	.99958	.99956	.99954
	110000	825.1	.99958	.99957	.99956	.99954	.99952
20.0	70000	525.0	.99974	.99973	.99971	.99969	.99966
	75000	562.5	.99972	.99971	.99969	.99967	.99964
	80000	600.0	.99970	.99969	.99967	.99965	.99963
	85000	637.6	.99969	.99967	.99966	.99964	.99961
	90000	675.1	.99967	.99966	.99964	.99962	.99959
	95000	712.6	.99965	.99964	.99962	.99960	.99958
	100000	750.1	.99963	.99962	.99960	.99958	.99956
	101325	760.0	.99963	.99961	.99960	.99958	.99956
	105000	787.6	.99961	.99960	.99958	.99957	.99954
	110000	825.1	.99959	.99958	.99957	.99955	.99953
21.0	70000	525.0	.99975	.99973	.99971	.99969	.99966
	75000	562.5	.99973	.99972	.99970	.99967	.99964
	80000	600.0	.99971	.99970	.99968	.99966	.99963
	85000	637.6	.99969	.99968	.99966	.99964	.99961
	90000	675.1	.99968	.99966	.99965	.99962	.99960
	95000	712.6	.99966	.99965	.99963	.99961	.99958
	100000	750.1	.99964	.99963	.99961	.99959	.99956
	101325	760.0	.99964	.99962	.99961	.99959	.99956
	105000	787.6	.99962	.99961	.99959	.99957	.99955
	110000	825.1	.99960	.99959	.99958	.99956	.99953
22.0	70000	525.0	.99975	.99974	.99972	.99969	.99966
	75000	562.5	.99974	.99972	.99970	.99968	.99964
	80000	600.0	.99972	.99971	.99969	.99966	.99963
	85000	637.6	.99970	.99969	.99967	.99964	.99961
	90000	675.1	.99968	.99967	.99965	.99963	.99960
	95000	712.6	.99967	.99965	.99963	.99961	.99958
	100000	750.1	.99965	.99964	.99962	.99960	.99957
	101325	760.0	.99965	.99963	.99961	.99959	.99956
	105000	787.6	.99963	.99962	.99960	.99958	.99955
	110000	825.1	.99962	.99960	.99958	.99956	.99954

Table 2 (Continued)

Temperature (Celsius)	Pressure (pascals)	(mm Hg)	Relative Humidity in Percent				
			0	25	50	75	100
23.0	70000	525.0	.99976	.99975	.99972	.99969	.99966
	75000	562.5	.99974	.99973	.99971	.99968	.99964
	80000	600.0	.99973	.99971	.99969	.99966	.99963
	85000	637.6	.99971	.99969	.99967	.99965	.99962
	90000	675.1	.99969	.99968	.99966	.99963	.99960
	95000	712.6	.99968	.99966	.99964	.99962	.99959
	100000	750.1	.99966	.99964	.99962	.99960	.99957
	101325	760.0	.99965	.99964	.99962	.99960	.99957
	105000	787.6	.99964	.99963	.99961	.99958	.99956
	110000	825.1	.99963	.99961	.99959	.99957	.99954
24.0	70000	525.0	.99977	.99975	.99973	.99969	.99965
	75000	562.5	.99975	.99973	.99971	.99968	.99964
	80000	600.0	.99973	.99972	.99970	.99967	.99963
	85000	637.6	.99972	.99970	.99968	.99965	.99962
	90000	675.1	.99970	.99969	.99966	.99964	.99960
	95000	712.6	.99968	.99967	.99965	.99962	.99959
	100000	750.1	.99967	.99965	.99963	.99961	.99957
	101325	760.0	.99966	.99965	.99963	.99960	.99957
	105000	787.6	.99965	.99964	.99962	.99959	.99956
	110000	825.1	.99964	.99962	.99960	.99957	.99954
25.0	70000	525.0	.99977	.99976	.99973	.99970	.99965
	75000	562.5	.99976	.99974	.99971	.99968	.99964
	80000	600.0	.99974	.99972	.99970	.99967	.99963
	85000	637.6	.99973	.99971	.99968	.99965	.99962
	90000	675.1	.99971	.99969	.99967	.99964	.99960
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	101325	760.0	.99967	.99966	.99963	.99961	.99957
	105000	787.6	.99966	.99964	.99962	.99960	.99956
	110000	825.1	.99965	.99963	.99961	.99958	.99955
26.0	70000	525.0	.99978	.99976	.99973	.99970	.99965
	75000	562.5	.99976	.99975	.99972	.99968	.99964
	80000	600.0	.99975	.99973	.99970	.99967	.99963
	85000	637.6	.99973	.99971	.99969	.99966	.99961
	90000	675.1	.99972	.99970	.99967	.99964	.99960
	95000	712.6	.99970	.99968	.99966	.99963	.99959
	100000	750.1	.99969	.99967	.99964	.99961	.99958
	101325	760.0	.99968	.99966	.99964	.99961	.99957
	105000	787.6	.99967	.99965	.99963	.99960	.99956
	110000	825.1	.99966	.99964	.99961	.99959	.99955

Table 2 (Continued)

Temperature (Celsius)	Pressure (Pascals)	(mm Hg)	Relative Humidity in Percent 0	25	50	75	100
27.0	70000	525.0	.99979	.99977	.99974	.99969	.99964
	75000	562.5	.99977	.99975	.99972	.99968	.99963
	80000	600.0	.99976	.99974	.99971	.99967	.99962
	85000	637.6	.99974	.99972	.99969	.99966	.99961
	90000	675.1	.99973	.99971	.99968	.99964	.99960
	95000	712.6	.99971	.99969	.99966	.99963	.99959
	100000	750.1	.99970	.99968	.99965	.99962	.99958
	101325	760.0	.99969	.99967	.99965	.99961	.99957
	105000	787.6	.99968	.99966	.99964	.99960	.99956
	110000	825.1	.99966	.99965	.99962	.99959	.99955
28.0	70000	525.0	.99979	.99977	.99974	.99969	.99964
	75000	652.5	.99978	.99976	.99972	.99968	.99963
	80000	600.0	.99976	.99974	.99971	.99967	.99962
	85000	637.6	.99975	.99973	.99970	.99966	.99961
	90000	675.1	.99973	.99971	.99968	.99965	.99960
	95000	712.6	.99972	.99970	.99967	.99963	.99959
	100000	750.1	.99970	.99968	.99966	.99962	.99958
	101325	760.0	.99970	.99968	.99965	.99962	.99957
	105000	787.6	.99969	.99967	.99964	.99961	.99956
	110000	825.1	.99967	.99965	.99963	.99959	.99955

In the absence of values for virial coefficients for air-CO_2 mixtures in the temperature range of interest, the effect of the variability of CO_2 abundance on Z has been estimated, by two methods, to be of the order of 1 p.p.m. and, therefore, negligible. Also, the effect of the variability of CO_2 abundance on Z due to the interaction of CO_2 with water vapor has been estimated to be of the order of 0.1 p.p.m. and, therefore, negligible. Consequently, table 2 is applicable to air containing reasonable amounts of CO_2.

For temperatures and/or pressures outside the range of table 2, the table of compressibility factor of moist air (also CO_2-free) in the Smithsonian Meteorological Tables [14] can be used, with some loss of precision since the listing there is just to the fourth decimal place.

3.4 Ratio of the Molecular Weight of Water to the Molecular Weight of Dry Air, ε

The molecular weight of water is 18.0152 [6]. The ratio, ε, of the molecular weight of water to that of dry air is, therefore, 0.62201 for dry air with a CO_2 mole fraction of 0.00033.

11

4. UNCERTAINTY IN CALCULATION OF AIR DENSITY

In estimating uncertainties we shall report them as 1 standard deviation and we shall follow the suggested practice of Eisenhart [12, 13] in stating separately the random and systematic components.

4.1 Uncertainty in R

The estimates of the uncertainties in the molar gas constant are based on the work of Quinn, Colclough and Chandler [3]. Their quoted random uncertainty is $\pm$ 0.17 JK^{-1} $kmol^{-1}$, which is $\pm$ 2.0 x 10^{-5}. The systematic uncertainties combined in quadrature results in an "overall systematic uncertainty of 17 p.p.m."

4.2 Uncertainties in M_a

The uncertainty in the O_2 abundance (mole fraction) of air [7] is separable into a random component and a systematic component. The random uncertainty is estimated to be $\pm$ 0.00001, the systematic component is $\pm$ 0.00006.

The random component of the uncertainty in the argon abundance is inferred from the precision of Hughes' measurements [9] to be $\pm$ 0.00001. No assignment of systematic uncertainty was made by Hughes.

The uncertainty in the CO_2 abundance has been mentioned earlier with respect to the variability of the CO_2 abundance in the laboratory. For a sample of air taken at the time a mass comparison is made, the uncertainty in the subsequent mass spectrometric determination of CO_2 abundance is $\pm$ 0.00003 at the 0.00033 level. Since the measurements made by the mass spectrometric method are considered to be very precise, the estimated uncertainty is considered to be systematic.

Since the N_2 abundance is the difference between unity and the sum of the mole fractions of the other constituents, the random component of the uncertainty in the N_2 abundance is found by combining by quadrature the random components of the uncertainties of the other three major components to be 1 x 10^{-5}. For the systematic component, however, the practice of finding the N_2 abundance by difference provides for very significant cancellation of uncertainties. This is shown in the following treatment.

Eq. (15) can be written:

$$M_a = M_{O_2} x_{O_2} + M_{CO_2} x_{CO_2} + M_A x_A + M_{N_2} x_{N_2} + \sum_{i=5}^{k} M_i x_i . \qquad (28)$$

The mole fraction of N_2 is, by difference,

$$x_{N_2} = 1 - x_{O_2} - x_{CO_2} - x_A - \sum_{i=5}^{k} x_i \quad . \tag{29}$$

If we ignore the last term in Eq. (28), differentiate and go to finite differences,

$$\Delta(M_a)_{x_i} = M_{O_2} \Delta x_{O_2} + M_{CO_2} \Delta x_{CO_2} + M_A \Delta x_A + M_{N_2}(- \Delta x_{O_2} - \Delta x_{CO_2} - \Delta x_A)$$

$$= (M_{O_2} - M_{N_2}) \Delta x_{O_2} + (M_{CO_2} - M_{N_2}) \Delta x_{CO_2} + (M_A - M_{N_2}) \Delta x_A \quad . \tag{30}$$

With the substitution of the appropriate systematic uncertainties and the molecular weights into Eq. (30), the systematic component of the relative uncertainty in M_a due to uncertainties in abundance of the constituents is found to be $\pm$ 3 x 10^{-5}. The random component of the relative uncertainty is found to be $\pm$ 2 x 10^{-5} by combining by quadrature the product of the molecular weight and the random component of uncertainty in abundance for each of the four major constituents and dividing by M_a.

The uncertainty in M_a due to the uncertainty in the value of the atomic or molecular weights of the i-th constituent is

$$\Delta(M_a)_{M_i} = x_i \, \Delta M_i \quad . \tag{31}$$

The uncertainties in the values of the atomic or molecular weights are inferred from reference [6][1]. For the four major constituents they are: for O_2, $\pm$ 0.0002; for CO_2, $\pm$ 0.0005; for A, $\pm$ 0.001; and for N_2, $\pm$ 0.0001. These uncertainties are considered to be systematic. The sum of the four terms represented by Eq. (31) is $\pm$ 0.0001, corresponding to a relative uncertainty in M_a of 4 x 10^{-6}.

The random component of the overall relative uncertainty in M_a is, by quadrature, $\pm$ 2 x 10^{-5}. The systematic component of the overall relative uncertainty in M_a is $\pm$ 3 x 10^{-5}, the sum of the component due to the systematic uncertainty in abundance and that due to the uncertainty in atomic or molecular weight. The corresponding random and systematic components of the relative uncertainty in ρ are $\pm$ 2 x 10^{-5} and $\pm$ 3 x 10^{-5}, respectively.

4.3 Uncertainty in Z

The uncertainty in Z, the compressibility factor, is estimated from the various uncertainties in Z due to the uncertainties in the virial coefficients [15]. The dominant uncertainty is that assigned to B_{aa} (one of the three used in the calculation of B_{mix} of Eq. (24) [11]), the second virial coefficient expressing the effects of interaction between two air

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1 The uncertainty assigned in the reference is divided by 3 to estimate the uncertainty at 1 standard deviation.

molecules. The estimated relative uncertainty in Z at 293.15K, 101325 Pa (1 atmosphere) and relative humidity 50 percent is $\pm$ 1.7 x 10^{-5}. The corresponding relative uncertainty, taken to be systematic, in ρ is $\pm$ 1.7 x 10^{-5}.

4.4 Uncertainty in ϵ

The uncertainty in M_e, the molecular weight of water, is $\pm$ 0.0005 [6] and is treated here as systematic. The uncertainty in ϵ, the ratio of M_e to M_a, is given by

$$\Delta\epsilon = \frac{M_a \Delta M_e - M_e \Delta M_a}{(M_a)^2} \quad . \tag{32}$$

The random component of $\Delta\epsilon$ thus calculated is $\pm$ 1 x 10^{-5} and the systematic component is $\pm$ 8 x 10^{-6}. The corresponding uncertainties in the factor in Eq. (14) involving ϵ,

$$\left[1 + (\epsilon-1)\frac{e'}{p} \right] , \tag{33}$$

at 293.15K, 101325 Pa and 50 percent relative humidity are $\pm$ 1 x 10^{-7} and $\pm$ 9 x 10^{-8}, respectively. The corresponding relative uncertainties in the term and consequently in ρ are $\pm$ 1 x 10^{-7} and $\pm$ 9 x 10^{-8}, respectively.

4.5 Combined Relative Uncertainties in ρ Due to the Uncertainties in M_a, R, Z and ϵ

The random and systematic components of the relative uncertainty in ρ at 293.15K, 101325 Pa and 50 percent relative humidity, due to the uncertainties in M_a, R, Z and ϵ are tabulated in table 3.

TABLE 3   RANDOM AND SYSTEMATIC COMPONENTS OF THE RELATIVE
UNCERTAINTY IN ρ CONTRIBUTED BY M_a, R, Z and ϵ
(at 293.15K, 101325 Pa and 50 percent relative
humidity)

Parameter	Random	Systematic
M_a	$\pm$ 2 x 10^{-5}	$\pm$ 3 x 10^{-5}
R	$\pm$ 2 x 10^{-5}	$\pm$ 1.7 x 10^{-5}
Z	--------	$\pm$ 1.7 x 10^{-5}
ϵ	$\pm$ 1 x 10^{-7}	$\pm$ 9 x 10^{-8}
Combined	$\pm$ 3 x 10^{-5}	$\pm$ 6 x 10^{-5}

The random components were combined by quadrature, the systematic components were combined by addition. These components of uncertainty can be considered to represent the uncertainty "intrinsic" to the air density equation, that is, that which is contributed by the limitations on the present knowledge of M_a, M_e, R and Z. With these uncertainties must, of course, be combined the uncertainties in the environmental variables: P, T and relative humidity, and in the knowledge of the carbon dioxide abundance.

5. MEASUREMENT OF P, T AND RELATIVE HUMIDITY

In order to estimate the uncertainties in ρ due to uncertainties in the measurements of the environmental variables, P, T and relative humidity, we shall estimate the uncertainties in these measurements when made using the best applicable instrumentation and procedures. Therefore, the estimated uncertainties in ρ will be those contributed by the best possible measurements.

5.1 Pressure Measurement

The state-of-the-art in pressure measurement [16] permits the measurement of the pressure in a laboratory with a random relative uncertainty of less than $\pm$ 2 X 10^{-4}. Calibration of pressure measuring instruments against a primary standard of pressure contributes a systematic relative uncertainty of about $\pm$ 3 x 10^{-5}. The corresponding $\Delta\rho/\rho$'s contributed by uncertainties in the measurement of pressure in a laboratory in the vicinity of a balance case are $\pm$ 2 x 10^{-4} and $\pm$ 3 x 10^{-5}.

5.2 Temperature Measurement

The measurement of temperature in a balance case, that is the temperature which determines the buoyant forces, is potentially the most critical measurement in terms of its effect on the uncertainty in the calculated air density. In the absence of experimental results, it is possible at this time to make only a rough estimate of the temperature uncertainty to be expected. If the balance case were instrumented with a network of thermopile junctions, for example, the measurements would be expected to have a standard deviation of about $\pm$ 0.05K [17]. The systematic uncertainty is estimated to be of the order of $\pm$ 0.01K. At a temperature of 293.15K, these uncertainties correspond to relative uncertainties of $\pm$ 2 x 10^{-4}, and $\pm$ 3 x 10^{-5}, respectively. The corresponding $\Delta\rho/\rho$'s are $\pm$ 2 x 10^{-4} and $\pm$ 3 x 10^{-5}.

5.3 Humidity Measurement

The state-of-the-art in humidity measurement [18] permits the measurement of humidity in a balance case with a random uncertainty of $\pm$ 0.5 percent relative humidity and a systematic uncertainty of $\pm$ 0.3 percent relative humidity. These uncertainties correspond to relative uncertainties in the

water vapor pressure factor $[1 + (\epsilon-1)e'/P]$, in Eq. (14) and, therefore, to $\Delta \rho / \rho$, of $\pm 4 \times 10^{-5}$ and $\pm 3 \times 10^{-5}$ at 293.15K, 101325 Pa and 50 percent relative humidity.

Since e' is the effective vapor pressure of water in <u>moist air</u>, a word of caution with regard to inferring e' from measurements of relative humidity is in order. Relative humidity, RH, can be defined [19] by

$$RH = \frac{e'}{e'_s} \times 100 \text{ percent},\qquad (34)$$

where e'_s is the <u>effective</u> saturation vapor pressure of water in moist air. e'_s is greater than e_s, the saturation vapor pressure of pure phase (i.e., water vapor without the admixture of air or any other substance) over a plane surface of pure ordinary liquid water, since the introduction of a second gas (air in this case) over the surface of the water increases the saturation concentration of water vapor above the surface of the water. This "enhancement" of water vapor pressure is expressed by the enhancement factor, f, which is defined by

$$f = \frac{e'_s}{e_s}\,.\qquad (35)$$

The most recently published [15] experimentally derived value of f at 293.15K and 100000 Pa is 1.00400. Therefore, the common practice of inferring e' from measured RH and tabulated values of e_s introduces a significant error in e' if f has been ignored. The corresponding relative error in ρ at 293.15K, 101325 Pa and 50 percent relative humidity is about 1.7×10^{-5}. f is a function of temperature and pressure.

In the present work, Hyland's values of f [15] have been fitted to a three-parameter equation in the pressure and temperature (t, °C) ranges of interest in national standards laboratories. The resulting equation is

$$f = 1.00070 + 3.113 \times 10^{-8} P + 5.4 \times 10^{-7} t^2.\qquad (36)$$

Values of f calculated using equation (36), tabulated in table 4, are in agreement with Hyland's values and are therefore appropriate for the present application.

The expression for e' is found by combining Eqs. (34) and (35) to be

$$e' = \frac{RH}{100} f\, e_s\,.\qquad (37)$$

The systematic relative uncertainties in ρ due to the uncertainties assigned to f [15] and e_s [22] are approximately 1×10^{-6} and 2×10^{-7}, respectively, and would be negligible whether f and e_s were treated as parameters or with the environmental variables.

TABLE 4. VALUES OF ENHANCEMENT FACTOR, f, CALCULATED
USING EQUATION (36)

Pressure, pascals	t, C			
	15	20	25	30
70 000	1.0030	1.0031	1.0032	1.0034
75 000	1.0032	1.0033	1.0034	1.0035
80 000	1.0033	1.0034	1.0035	1.0037
85 000	1.0035	1.0036	1.0037	1.0038
90 000	1.0036	1.0037	1.0038	1.0040
95 000	1.0038	1.0039	1.0040	1.0041
100 000	1.0039	1.0040	1.0042	1.0043
101 325	1.0040	1.0041	1.0042	1.0043
105 000	1.0041	1.0042	1.0043	1.0045
110 000	1.0043	1.0043	1.0045	1.0046

For the temperature range of interest in the present application, any of
several tables of e_s, for example, references [21], [22], and [23], can
be used. Besley and Bottomley [24] have recently published experimental
values of e_s in the temperature range 272.60 to 298.04K.

Values of e_s in the temperature range of interest for standards laboratories,
have been calculated using the formulation of Wexler and Greenspan [22]
and are tabulated in table 5.

TABLE 5 VALUES OF SATURATION WATER VAPOR PRESSURE, e_s,
CALCULATED USING FORMULATION OF WEXLER AND
GREENSPAN [22]

e_s, Pascals

Temperature, C

	15	16	17	18	19	20	21	22	23	24	25	26	27
.00	1705	1818	1938	2064	2197	2338	2487	2644	2810	2985	3169	3363	3567
.05	1711	1824	1944	2070	2204	2346	2495	2652	2818	2994	3178	3372	3577
.10	1716	1830	1950	2077	2211	2353	2503	2660	2827	3003	3188	3382	3588
.15	1722	1836	1956	2083	2218	2360	2510	2669	2836	3012	3197	3392	3598
.20	1727	1841	1962	2090	2225	2367	2518	2677	2844	3021	3207	3402	3609
.25	1733	1847	1968	2097	2232	2375	2526	2685	2853	3030	3216	3413	3619
.30	1738	1853	1975	2103	2239	2382	2533	2693	2861	3039	3226	3423	3630
.35	1744	1859	1981	2110	2246	2390	2541	2701	2870	3048	3235	3433	3641
.40	1749	1865	1987	2116	2253	2397	2549	2709	2879	3057	3245	3443	3651
.45	1755	1871	1994	2123	2260	2404	2557	2718	2887	3066	3255	3453	3662

Table 5 (Continued)

e_s, pascals

Temperature, C

	15	16	17	18	19	20	21	22	23	24	25	26	27
.50	1761	1877	2000	2130	2267	2412	2565	2726	2896	3075	3264	3463	3673
.55	1766	1883	2006	2136	2274	2419	2573	2734	2905	3085	3274	3473	3683
.60	1772	1889	2012	2143	2281	2427	2580	2743	2914	3094	3284	3484	1694
.65	1778	1895	2019	2150	2288	2434	2588	2751	2922	3103	3294	3494	3705
.70	1783	1901	2025	2157	2295	2442	2596	2759	2931	3112	3303	3504	3716
.75	1789	1907	2032	2163	2302	2449	2604	2768	2940	3122	3313	3515	3727
.80	1795	1913	2038	2170	2310	2457	2612	2776	2949	3131	3323	3525	3738
.85	1801	1919	2044	2177	2317	2464	2620	2785	2958	3140	3333	3535	3749
.90	1806	1925	2051	2184	2324	2472	2628	2793	2967	3150	3343	3546	3759
.95	1812	1931	2057	2190	2331	2480	2636	2801	2976	3159	3353	3556	3770

In the present work, the data of Besley and Bottomley in the temperature range 288.15 to 298.15K and calculated values [22] for the remainder of the temperature range to 301.15K, have been fitted to a two-parameter equation. The resulting equation is

$$e_s = 1.7526 \times 10^{11} \exp(-5315.56/T). \qquad (38)$$

Values calculated using equation (38) are sufficiently close to experimental values and values calculated by the more complex formulation, within $\pm$ 0.1 percent, to be used in the present application.

5.4 Random and Systematic Components of the Relative Uncertainty in ρ Due to Anticipated Uncertainties in State-of-the-Art Measurements of P, T and Relative Humidity

The random and systematic components of the relative uncertainty in ρ at 293.15K, 101325 Pa and 50 percent relative humidity due to anticipated uncertainties in state-of-the-art measurements of the environmental variables are tabulated in table 6.

TABLE 6: RANDOM AND SYSTEMATIC COMPONENTS OF THE RELATIVE UNCERTAINTY IN ρ DUE TO ANTICIPATED UNCERTAINTIES IN STATE-OF-THE-ART MEASUREMENTS OF P, T AND RELATIVE HUMIDITY (at 293.15K, 101325 Pa and 50 percent relative humidity)

Variable	Random	Systematic
P	$\pm 2 \times 10^{-4}$	$\pm 3 \times 10^{-5}$
T	$\pm 2 \times 10^{-4}$	$\pm 3 \times 10^{-5}$
Relative Humidity	$\pm 4 \times 10^{-5}$	$\pm 3 \times 10^{-5}$
Combined	$\pm 3 \times 10^{-4}$	$\pm 9 \times 10^{-5}$

The random components were combined by quadrature, the systematic components were combined by addition.

It is clear from inspection of tables 3 and 6 that the dominant uncertainty in the calculation of air density is that contributed by the measurement of pressure, temperature and relative humidity, even when the measurements are made using the best instrumentation and procedures. Considerable care must therefore be taken in making measurements of these environmental variables in order to attempt to approach the precision and accuracy represented in table 6.

To illustrate the effect of errors in measurement of the environmental variables, at 293.15K, 101325 Pa and 50 percent relative humidity (RH) an error of 0.1 percent in calculated air density results from an error of 0.29K in temperature measurement or a 101 Pa error in pressure measurement or an 11.3 percent RH error in the measurement of RH.

5.5 Carbon Dioxide Abundance

As stated in section 3.1, the CO_2 abundances in laboratory air and consequently in the air in balance cases is in general variable. A variation of 0.0001 in CO_2 mole fraction is equivalent to a relative variation of 4×10^{-5} in calculated air density. Consequently, for optimum utilization of the air density calculation, the CO_2 abundance should be known. Eq (23) enables convenient adjustment of M_a for departures from the reference level, 0.00033, of CO_2 abundance.

6. OVERALL UNCERTAINTY IN ρ DUE TO UNCERTAINTIES IN THE PARAMETERS AND VARIABLES IN THE AIR DENSITY EQUATION

The random and systematic components of the relative uncertainties in ρ tabulated in tables 3 and 6 when combined, provide estimates of the components of the overall relative uncertainty in ρ. The random component, by quadrature, is $\pm 3 \times 10^{-4}$; the systematic component, by addition, is $\pm 2 \times 10^{-4}$. The relative uncertainty due to the variation of CO_2 abundance (4×10^{-5} per 0.0001 in CO_2 mole fraction) is necessarily not included in this estimate.

These components of the overall uncertainty have been estimated at 293.15K, 101325 Pa and 50 percent relative humidity. They are based on the present knowledge of M_a, R, Z and ε and on estimates of the anticipated uncertainties in the measurements of the environmental variables (P, T and relative humidity) using the best applicable measurement instrumentation and procedures.

7. AIR DENSITY AT STANDARD CONDITIONS, ρ_0

The air density, ρ_0, at standard conditions (P_0, M_{a0}, R, T_0, Z_0), for dry air is expressed by an equation of the form of Eq. (14) as

$$\rho_0 = \frac{P_0 M_{a_0}}{RT_0 Z_0} \ . \tag{39}$$

By dividing Eq. (14) by Eq. (39) we arrive at

$$\rho = \rho_0 \left(\frac{P}{P_0}\right)\left(\frac{T_0}{T}\right)\left(\frac{Z_0}{Z}\right)\left(\frac{M_a}{M_{a_0}}\right)\left[1 + (\varepsilon-1)\frac{e'}{P}\right] \ . \tag{40}$$

The gas constant, R, has been eliminated but M_a has not unless the apparent molecular weight of the dry air in the standard state is equal to M_a. For example, if the ρ_0 is determined by experiment, M_{a_0} is not necessarily equal to M_a.

If an experimental value of ρ_0 of sufficient accuracy were available in the determination of which R was not used, R and its associated uncertainty would be eliminated. In the absence of such an experimental value, as is the present case, the use of an equation combining Eq. (14) with Eq. (23) is preferred to an equation of the form of Eq. (40).

If standard conditions are taken to be T_0 = 273.15K, P_0 = 101325 Pa, M_{a_0} = 28.963, and relative humidity = 0, for which Z_0 = 0.99940, ρ_0 is calculated by Eq. (14) to be 1.2928 kg m^{-3}. The same result is obtained for M_a = 28.964 (i.e., for a CO_2 mole fraction of 0.00043).

8. AIR DENSITY EQUATION

By combining Eq. (14) with Eq. (37) and substituting $\frac{M_w}{M_a}$ for ε, the air density equation developed in this work becomes

$$\rho = \frac{PM_a}{RTZ}\left[1 - \left(1 - \frac{M_w}{M_a}\right)\frac{RH}{100}\frac{f\ e_s}{P}\right] \ . \tag{41}$$

By substituting the QCC value of R, the value 18.0152 for M_w and by substituting the appropriate value, 28.963, for $M_{a_{033}}$ in Eq. (23), Eq. (41) becomes

$$\rho = 0.000120254 \frac{PM_a}{TZ}\left[1 - \left(1 - \frac{18.0152}{M_a}\right)\frac{RH}{100}\frac{f\ e_s}{P}\right] \ , \tag{42}$$

where

$$M_a = 28.963 + 12.011\left[x_{CO_2} - 0.00033\right] \ . \tag{43}$$

20

When SI units of pressure (Pa) and temperature (K) are used, the SI unit of density (kg m^{-3}) results. (The SI unit of density is, of course, equivalent to 10^{-3}g cm^{-3}.)

For T = 293.15K, P = 101325 Pa, RH = 50 percent and $M_{a_{0333}}$ = 28.963 g mol^{-1}, the air density calculated using Eq. (21) is 1.1991 kg m^{-3}.

8.1 Use of Constants in the Air Density Equation

In this section we shall investigate the effect on mass comparisons of the use of appropriate <u>constant</u> values of f, Z and M_a in Eq. (42).

The buoyant effect of the displacement of air by a mass artifact is proportional to the density of the air, ρ, and the displacement volume, V_m, of the artifact. We define here the buoyancy correction, m_b, to be added to the observed mass, by the following equation:

$$m_b \equiv \rho V_m = \rho \frac{m}{\rho_m} \,, \tag{44}$$

where $\underline{m}$ and $\underline{\rho_m}$ are the mass and density, respectively, of the artifact.

To estimate the variation, Δm_b, in m_b due to a relative uncertainty, $\Delta\rho/\rho$, in air density, Eq. (44) is differentiated with respect to ρ and the differentials are replaced by finite differences. The resulting equation can be written

$$\Delta m_b - \frac{m}{\rho_m} (\frac{\Delta\rho}{\rho}) \rho \,. \tag{45}$$

By substituting a nominal value of ρ, 1.2 mg cm^{-3}, in Eq. (45), we arrive at

$$\Delta m_b = 1.2 \frac{m}{\rho_m} (\frac{\Delta\rho}{\rho}) \,, \tag{46}$$

where $\underline{\Delta m_b}$ is in milligrams. We shall return to this equation to estimate the uncertainty in mass comparisons due to the use of certain constants in Eq. (42) for the calculation of air density.

To estimate the effect of a variation in f about a selected constant value, nominal values of P, T, M_a, Z, RH and e_s are substituted in Eq. (42) and the resulting equation is differentiated with respect to f. Nominal values appropriate to the Mass Laboratory of NBS are P = 100000 Pa, T = 298.15K, M_a = 28.964 g mol^{-1}, RH = 30 percent and e_s = 3169 Pa. The resulting equation is

$$\rho = 1.1686 (1 - 0.003594 \ f). \tag{47}$$

21

Differentiating Eq. (47) with respect to f, dividing the left and right sides of the resulting equation by ρ and f, and going to finite differences we find that

$$\frac{\Delta\rho}{\rho} = -0.003609 \frac{\Delta f}{f} \quad . \tag{48}$$

The values of f in table 4 range from 1.0030 to 1.0046, therefore the maximum $\Delta f/f$ for a nominal value of f of 1.0042 is equal to 1.2×10^{-3}. The corresponding $\Delta\rho/\rho$ is equal to 4.3×10^{-6}.

To estimate the effect of a variation of Z about a selected constant value, Eq. (42) is differentiated with respect to Z, the left and right sides of the resulting equation are divided by ρ and Z and finite differences are substituted for the partial differentials. The result is

$$\frac{\Delta\rho}{\rho} = \frac{-\Delta Z}{Z} \quad . \tag{49}$$

To estimate the expected variation in Z, it is necessary to estimate the ranges of the environmental variables, P, T and RH. The mean pressure in the Mass Laboratory at NBS is estimated to be 100106 Pa. The maximum and minimum of the atmospheric pressure at NBS, taken from climatological records of the National Weather Service of the National Oceanic and Atmospheric Administration and adjusted to the elevation of the Mass Laboratory, are 103850 and 96160 Pa. The expected ranges in temperature and relative humidity are taken to be 18 and 28C and 10 and 50 percent, respectively. For the nominal values given in this section, the expected variations in the environmental variables result in a variation of Z between 0.99957 and 0.99971. These extremes in Z correspond to relative variations in Z about the nominal value, 0.99966, of 9×10^{-5} and 5×10^{-5}, respectively. The corresponding $\frac{\Delta\rho}{\rho}$'s are -9×10^{-5} and -5×10^{-5}.

As was shown in section 3.2, a variation of 0.0001 in CO_2 mole fraction corresponds to a relative variation in M_a of 4×10^{-5} and to a $\Delta\rho/\rho$ of -4×10^{-5}.

Combining by quadrature the maximum values of $\Delta\rho/\rho$ due to expected variations in f and Z and variation of 0.0001 in CO_2 mole fraction, the result is 9.9×10^{-5}. This is the value to be used in Eq. (46). Since the values combined are maximum values, the combined value can be considered loosely to approximate 3 standard deviations.

For various materials of interest in the comparison of mass artifacts, Δm_b in micrograms (μg) has been calculated using Eq. (46) for 1 kg and 100 g artifacts and tabulated in table 7.

22

TABLE 7   VARIATION IN BUOYANCY CORRECTION (m_b)
           DUE TO EXPECTED VARIATIONS IN f, Z AND
           M_a IN MASS LABORATORY OF NBS

Material	ρ_m, g cm^{-3}	Δm_b, μg 1 kg	Δm_b, μg 100 g
Platinum-iridium	21.5	5.5	0.55
Stainless steel	8.0	15	1.5
Silicon	2.2	54	5.4
Brass	8.4	14	1.4
Aluminum	2.7	44	4.4
Tantalum	16.6	7.1	0.71
Water	1.0	119	12

We shall now apply Eq. (46) and table 7 to the comparison of mass artifacts. In the comparison of two mass artifacts of nearly equal mass, m, but different densities, ρ_1 and ρ_2, the apparent difference in mass, m_d, due to the difference in buoyant force on the two artifacts is given by

$$m_d = \rho(\rho_1 V_1) \left(\frac{1}{\rho_1} - \frac{1}{\rho_2}\right) \stackrel{\sim}{=} \rho m\left(\frac{1}{\rho_1} - \frac{1}{\rho_2}\right) , \qquad (50)$$

where V_1 is the displacement volume of the artifact of density ρ_1 and $\underline{\rho}$ is the air density.

By differentiating Eq. (50) with respect to ρ and going to finite differences, the resulting equation can be written

$$\Delta m_d \stackrel{\sim}{=} m\left(\frac{\Delta\rho}{\rho}\right) \left(\frac{1}{\rho_1} - \frac{1}{\rho_2}\right)\rho = \frac{m}{\rho_1} \left(\frac{\Delta\rho}{\rho}\right)\rho - \frac{m}{\rho_2} \left(\frac{\Delta\rho}{\rho}\right)\rho . \qquad (51)$$

Each of the terms on the right side of Eq. (51) is recognized to be Δm_b of Eq. (45). Therefore,

$$\Delta m_d \stackrel{\sim}{=} (\Delta m_b)_1 - (\Delta m_b)_2 , \qquad (52)$$

where the subscript numbers refer to materials of density ρ_1 and ρ_2. Thus the variation in the apparent difference in mass of two artifacts due to the difference in buoyant force on them, resulting from the use of constant values of f, Z and M_a is approximated by the difference between the Δm_b's in table 7 for the appropriate materials. For example, for a comparison of kilogram artifacts of platinum-iridium and stainless steel the variation, Δm_d, is 15 - 5.5 = 9.5 μg.

23

On the bases of the values of Δm_d calculated using table 7 and the precision of the balance used for mass comparisons, a judgment can be made concerning the adequacy of the use of constant values of f, Z and M_a in Eq. (42). The precision of the balance used for the comparisons of 1 kg mass artifacts at NBS is 25 µg at the 1 standard deviation level. Thus it can be concluded, for example, that constant values can be used in the comparison of platinum-iridium and stainless steel artifacts, and stainless steel and brass kilogram artifacts, but not for comparison of platinum-iridium and silicon kilogram artifacts. The precision of the kilogram balance at the Bureau International des Poids et Mesures (BIPM) is 1.5 µg at the 1 standard deviation level, therefore it could be concluded that the use of constants would not be appropriate in mass comparisons made using that balance.

For mass comparisons in the Mass Laboratory of NBS for which the values in table 7 indicate that the use of constant values of f (1.0042), Z (0.99966) and M_a (28.964) in Eq. (42) is adequate, the resulting equation is

$$\rho = \frac{0.0034842}{T} (P - 0.0037960 \ RH \ e_s). \qquad (53)$$

For pressure in millimeters of mercury and temperature, t, in $^\circ$C, Eq. (53) becomes

$$\rho = \frac{0.46452}{(t + 273.15)} (P - 0.0037960 \ RH \ e_s) \quad , \qquad (54)$$

where the SI units of density are equivalent to mg cm^{-3}.

e_s In millimeters of mercury is calculated using an equation of the form of Eq. (38) in which (t + 273.15) is substituted for T, and the preexponential factor is modified. The resulting equation is

$$e_s = 1.3146 \times 10^9 \exp (-5315.56/(t + 273.15)). \qquad (55)$$

Alternatively, the appropriate value of e_s in Pa could be taken from table 5 and multiplied by 0.00750062 to convert to millimeters of mercury.

9. SUMMARY AND CONCLUSIONS

An equation suitable for use in calculation of air density for air buoyancy determination in the transfer of the mass unit by comparison of two mass artifacts on a balance has been developed. The Quinn, Colclough and Chandler value of the gas constant, R, 8315.73 JK^{-1} kmol^{-1}, has been used in the formulation. The apparent molecular weight of dry air, M_a, has been calculated using currently accepted values of atomic weights and recent determinations of the abundances of the various constituents of air. The abundance of CO_2 has been treated as variable. A "background" value of mole fraction, 0.00033, has been used and a factor enabling convenient adjustment of M_a for deviation of CO_2 abundance from the background value has been

derived. A new table of compressibility factor, Z, for the range of pressure and temperature of interest in standards laboratories has been calculated using recently determined values of virial coefficients. The enhancement factor, f, which has usually been ignored in air density equations, has been included explicitly in the equation. A table of f has been calculated using a simple equation fitted to values of f in the range of pressure and temperature of interest. A table of the saturation vapor pressure of water, e_s, based on a formulation of Wexler and Greenspan has been included. A simple equation for the calculation of e_s has been fitted.

Uncertainties, random and systematic, in the parameters R, M_a, Z, and ϵ, the ratio of the molecular weight of water vapor to the molecular weight of dry air, and in the determination of the values of the environmental variables, pressure, temperature and water vapor pressure, in the air density equation have been estimated. The estimated random and systematic relative uncertainties, $\Delta\rho/\rho$, contributed by the parameters are $\pm 3 \times 10^{-5}$ and $\pm 6 \times 10^{-5}$, respectively. The relative uncertainties anticipated to be contributed by state-of-the-art measurements of the environmental variables are estimated to be $\pm 3 \times 10^{-4}$ random and $\pm 9 \times 10^{-5}$ systematic. The effect of an ignored deviation of CO_2 abundance from the "background" value would be an additional systematic relative uncertainty in ρ of $\pm 4 \times 10^{-5}$ per 0.0001 variation of CO_2 mole fraction. The estimated overall random and systematic relative uncertainties are $\pm 3 \times 10^{-4}$ and $\pm 2 \times 10^{-4}$, respectively.

At 293.15K, 101325 Pa (1 atmosphere), and 50 percent relative humidity, the estimated overall relative uncertainties in ρ correspond to uncertainties in mass in the transfer between platinum-iridium and stainless steel kilogram artifacts (volume difference of ~ 80 cm^3) of approximately 30 micrograms random and 20 micrograms systematic.

The following are recommendations concerning the transfer of the mass unit at the various national standards laboratories:

(1) Eq. (42) should be adopted for use for all national standards laboratories to provide both uniformity and the best available calculation of air density.

(2) The CO_2 concentration should be treated as a variable and at least a "background" value should be determined for each of the laboratories.

(3) Instrumentation and practices representing the state-of-the-art in the measurement of the environmental variables should be applied.

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11. REFERENCES

[1]   List, R. J., Smithsonian Meteorological Tables, (The Smithsonian
      Institution, Washington, D.C., 1951), 6th Revised Edition, p. 347.

[2]   Cohen, E. R., and Taylor, B. N., J. Phys. Chem. Ref. Data, 2, 663
      (1973).

[3]   Quinn, T. J., Colclough, A. R., and Chandler, T. R. D., Phil. Trans.
      Royal Society of London A283, 367 (1976).

[4]   Gammon, B. E., J. Chem. Phys. 64, 2556 (1976).

[5]   Gammon, B. E., private communication.

[6]   International Union of Pure and Applied Chemistry, Inorganic Chemis-
      try Division, Commission on Atomic Weights, Pure and Appl. Chem. 47,
      75 (1976).

[7]   Machta, L., and Hughes, E., Science 168, 1582 (1970).

[8]   Gluekauf, E., in Compendium of Meteorology, T. F. Malone, Editor,
      (The American Meteorological Society, Boston, Mass., 1951), p. 4.

[9]   Hughes, E. E., A Mass Spectrometric Technique for the Accurate
      Determination of Atmospheric Argon, ACS 4th Mid-Atlantic Meeting,
      Washington, D.C., Feb. 13, 1969, unpublished.

[10] U.S. Standard Atmosphere, 1962, (U.S. Government Printing Office
      Washington, D.C., 1962), p. 9.

[11] Hyland, R. W., and Wexler, A., J. Res. Nat. Bur. Stand. (U.S.),
      77A, 133 (1973).

[12] Eisenhart, C., J. Res. Nat. Bur. Stand. (U.S.), 67C, 161 (1963).

[13] Eisenhart, C., Science 160, 1201 (1968).

[14] List, R. J., loc. cit., p. 333.

[15] Hyland, R. W., J. Res. Nat. Bur. Stand. (U.S.), 79A, 551 (1975).

[16] Heydemann, P. L. M., private communication.

[17] Roeser, W. F. and Wensel, H. T., in Temperature, Its Measurement
      and Control in Science and Industry, American Institute of Physics,
      National Bureau of Standards, National Research Council (Reinhold
      Publishing Corp., New York, 1941), p. 311.

[18] Wexler, A., Meteorological Monographs 11, 262 (1970).

[19]   Harrison, L.P., in Humidity and Moisture, Vol. III, A. Wexler, and W. A. Wildhack, Editors, (Reinhold Publishing Corp., New York, 1964), p. 51.

[20]   Greenspan, L., J. Res. Nat. Bur. Stand. (U.S.), 80A, 41 (1976).

[21]   List, R. J., loc. cit., p. 352.

[22]   Wexler, A. and Greenspan, L., J. Res. Nat. Bur. Stand. (U.S.), 75A, 213 (1971).

[23]   Ambrose, D. and Lawrenson, I. J., J. Chem. Thermodynamics 4, 755 (1972).

[24]   Besley, L., and Bottomley, G. A., J. Chem. Thermodyanmics 5, 397 (1973).